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## Theoretical study of equilibrium and nonequilibrium exciton dynamics in disordered semiconductors

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We develop a temperature-dependent theory for singlet exciton hopping transport in disordered semiconductors. It draws on the transport level concept within a Förster transfer model and bridges the gap in describing the transition from equilibrium to nonequilibrium time-dependent spectral diffusion. We test the validity range of the developed model using kinetic Monte Carlo simulations and find agreement over a broad range of temperatures. It reproduces the scaling of the diffusion length and spectral shift with the dimensionless disorder parameter and describes in a unified manner the transition from equilibrium to nonequilibrium transport regime. We find that the diffusion length in the nonequilibrium regime does not scale with the the third power of the Förster radius. The developed theory provides a powerful tool for interpreting time-resolved and steady state spectroscopy experiments in a variety of disordered materials, including organic semiconductors and colloidal quantum dots.

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### I. INTRODUCTION

The phenomenon of exciton diffusion is found to play a role in a remarkably wide range of physical systems, including disordered organic semiconductors [1,2], nanocrystalline quantum dots [3–6], semiconducting carbon nanotubes [7–10], and photosynthetic biological systems [11]. Moreover, there is a growing interest in describing electronic excitation energy transfer because exciton dynamics determines function in many technological applications. For example, in thin-film organic solar cells, exciton diffusion drives charge separation [12,13], in organic light emitting diodes it determines the brightness and color of the device [14], in scintillator detectors it controls the response function and yield [15], while in quantum communication systems it facilitates photon antibunching [16].

In disordered semiconductors that display weak intermolecular interactions, excitations created upon light absorption, carrier recombination, or annihilation processes are typically Frenkel excitons that are localized on single chromophore units (molecule, conjugated segment, quantum dot) and have a finite lifetime before relaxation to the ground electronic state occurs by radiative or nonradiative process. In the weak coupling regime, excitons transfer from one unit to the other with a Markovian incoherent hopping process and transport can be described as a simple diffusive motion [17]. However, chromophore units are not equivalent to each other as they can have different on-site excitation energies due to the different local environment, structure, or size as well as different excitonic couplings with neighbors. As a consequence, the

energy landscape has a distribution that is often approximated by a Gaussian [18] and the standard deviation of the distribution defines the disorder parameter  $\sigma$ . Therefore, in the course of time, excitations sample the energetic landscape and on average relax to lower energy sites until they “settle down” to a steady state and equilibrium is achieved. However, because excitations have a finite lifetime  $\tau$ , the relaxation process might be incomplete and, consequently, the exciton transport out of equilibrium [19]. It should be emphasized that this spectral relaxation process is different from the initial rapid vibronic relaxation [20]. Another consequence of the finite lifetime is that excitations have a limited spatial diffusion range, determined by the diffusion length  $L_D$  [19,21,22]. Spectroscopic techniques such as time-resolved and time-integrated photoluminescence spectroscopy can provide information on spectral diffusion [23–25] and a number of organic and inorganic systems have been studied over a range of temperatures [26–31].

A common misconception exists, that in practical device applications at room temperature, equilibrium transport prevails and the description of transport in terms of normal diffusion is sufficient. However, the distinction between equilibrium and nonequilibrium exciton transport is quite a subtle one and the transport regime is not uniquely defined only by temperature. Whilst significant progress has been made on understanding temperature dependent spectral relaxation and exciton diffusion, including experimental measurements [26–33] and computational models [19,21,33–44], currently there is no analytical theory that can describe the transition from equilibrium to nonequilibrium transport. In contrast, for charges it has been suggested that the transport problem can be modeled as a multiple-trapping process and it has been shown that a unique level in the energy distribution exists, the transport energy (TE), that plays the same role as the

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mobility edge in the multiple-trapping mechanism [45–47]. Note that in contrast to the long-range nature of the dipole-dipole interaction facilitating singlet exciton transport [48], charge transport in disordered semiconductors occurs via a short-range tunneling mechanism [49].

In this paper, we shall develop and test a theory that can treat the dynamics of exciton diffusion at both the equilibrium and nonequilibrium transport regime. In what follows, we develop a formalism based on the TE concept for the calculation of singlet exciton transport parameters, such as relaxation energy and diffusivity, including their temporal dependence. The validity of the TE level concept for Förster processes has been demonstrated by Baranovskii and Faber [50]. However, the TE level concept has not been applied yet to describe temperature and time dependent singlet exciton transport. In Sec. II, we repeat the main arguments and equations of Ref. [50] to enable the reader to follow theoretical consideration in Sec. III based on these equations. Section III includes the main results (Secs. III A, B, and E) along with a comparison of the theory to Monte Carlo simulations (Sec. III C), a discussion on the TE level concept for short vs long-range transfer and comparison with experiments (Sec. III D). Section IV summarizes the work and draws conclusions.

## II. TRANSPORT ENERGY LEVEL FOR FÖRSTER TRANSFER

We consider thermally assisted Förster energy transfer between localized states described by the rate [19,50,51]

$$v(\varepsilon_d \rightarrow \varepsilon_a) = \frac{1}{\tau} S(R) \exp\left[-\frac{\Delta\varepsilon + |\Delta\varepsilon|}{2k_B T}\right], \quad (1)$$

with

$$S(R) = \left(\frac{R_F}{R}\right)^6, \quad (2)$$

where  $\tau$  is the intrinsic exciton lifetime,  $R_F$  is the Förster radius, determined by the donor-acceptor spectral overlap, and  $k_B T$  is the thermal energy.  $\Delta\varepsilon = \varepsilon_a - \varepsilon_d$  is the difference between the donor and acceptor energies and  $R$  is the corresponding distance.

We take into account a Gaussian distribution of energy states  $g(\varepsilon) = N/\sqrt{2\pi\sigma^2} \exp(-\varepsilon^2/2\sigma^2)$ , with  $N$  and  $\sigma$  the total density of states (DOS) and the width of the distribution, respectively. If the relaxation process is completed during the lifetime  $\tau$ , excitons will occupy states around the equilibrium energy  $\varepsilon_\infty$  (see Fig. 1) at which the product  $g(\varepsilon)f(\varepsilon, \varepsilon_F)$  maximizes [49]. Here,  $f(\varepsilon, \varepsilon_F) = \{1 + \exp[(\varepsilon - \varepsilon_F)/k_B T]\}^{-1}$  is the Fermi distribution and  $\varepsilon_F$  is the Fermi level, determined by the number density  $n$  of the excitons as

$$n = \int_{-\infty}^{+\infty} g(\varepsilon)f(\varepsilon, \varepsilon_F)d\varepsilon. \quad (3)$$

Note that at low densities, the equilibrium energy  $\varepsilon_\infty$  can be approximated by either  $-\sigma^2/k_B T$ , at high temperatures [52], or by  $\varepsilon_F$ , at low temperatures; see Fig. 2(a).

Now, we examine the possibility of the existence of a TE level  $\varepsilon_{tr}$  in the energy distribution that can serve as the mobility edge in our exciton diffusion problem [50]. In the presence of such an energy level, excitons with  $\varepsilon > \varepsilon_{tr}$ , will, on average,

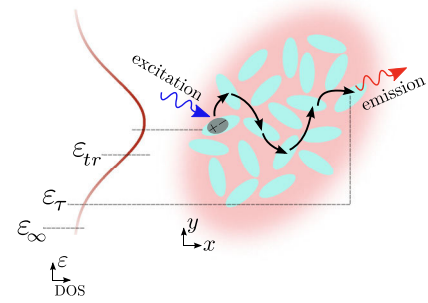


FIG. 1. Schematic illustration of interacting units in a disordered semiconductor, resulting in a Gaussian broadened excitonic DOS. Singlet exciton diffusion via Förster-type energy transfer process triggers energy relaxation toward the equilibrium energy  $\varepsilon_\infty$ . Due to the finite lifetime, excitons may decay at a higher energy,  $\varepsilon_\tau$ .  $\varepsilon_{tr}$  is the transport energy level.

move downward in the distribution, toward the TE level. On the other hand, upward jumps of excitons with  $\varepsilon < \varepsilon_{tr}$  will be in the vicinity of  $\varepsilon_{tr}$ . If we express the mean jump distance as

$$R_{\varepsilon_{tr}} = \left[ \frac{4\pi}{3} \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon)f'(\varepsilon, \varepsilon_F)d\varepsilon \right]^{-1/3}, \quad (4)$$

we can obtain the following equation governing the position of the TE level for the Förster transport problem:

$$g(\varepsilon_{tr})f'(\varepsilon_{tr}, \varepsilon_F) = \frac{1}{2k_B T} \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon)f'(\varepsilon, \varepsilon_F)d\varepsilon, \quad (5)$$

where  $f'(\varepsilon, \varepsilon_F) = 1 - f(\varepsilon, \varepsilon_F)$ . We have used the approach of Ref. [46] to obtain the above equation, according to which one can find  $\varepsilon_{tr}$  by maximizing the upward transfer rate; see Appendix A for more details. We emphasize that the form of Eq. (5) directly follows from the inverse sixth power distance dependence of the dipole-dipole interaction. Equation (5) also shows that the position of  $\varepsilon_{tr}$  is independent of the characteristic length  $R_F$  and the density  $N$ , in contrast to the charge transport problem in which  $\varepsilon_{tr} = \varepsilon_{tr}(\alpha, N)$ . Interestingly, Eq. (5) does not acquire a solution for an exponential DOS. Again, this is in contrast to the charge transport problem, where for both Gaussian and exponential DOS one can find a TE level in the energy distribution. Charge transport in disordered semiconductors occurs via short-range transfer mechanism, with a rate similar to Eq. (1), but with  $S(R) = \exp(-2R/\alpha)$ , where  $\alpha$  is the carrier localization length.

Figure 2(a) illustrates  $\varepsilon_{tr}$  as a function of disorder normalized thermal energy. At high temperatures,  $\varepsilon_{tr}$  lies near the center of the energy distribution. At lower temperatures,  $\varepsilon_{tr}$  decreases to lower energies because by decreasing the temperature thermal activation to higher energies becomes less probable. We point out that a meaningful application of the TE level requires that the condition  $\varepsilon_{tr} > \varepsilon_\infty$  [49] is satisfied. To test this condition, we plot a heat map of  $\varepsilon_{tr} - \varepsilon_\infty$  as a function of  $k_B T/\sigma$  and excitation density in Fig. 2(b), which shows that this condition is fulfilled over a broad range of temperatures and exciton densities. Thus the concept of the TE can be used for Förster-type exciton transport. In what follows, we consider the weak excitation condition, with  $n/N \ll 1$  and therefore  $f' \approx 1$ . More precisely, we use  $\sigma = 0.065$  eV,  $N = 1$  nm<sup>-3</sup> and

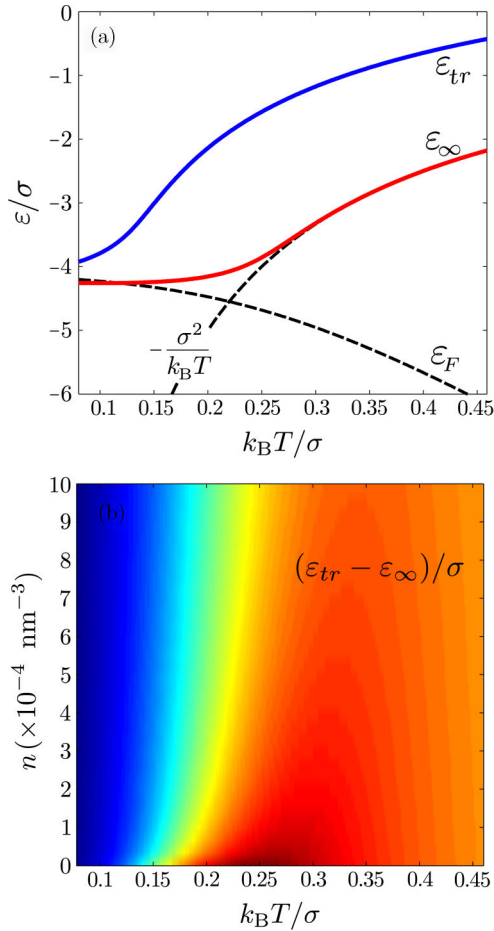


FIG. 2. (a) Transport energy level  $\varepsilon_{tr}$ , as a function of disorder normalized temperature. Data are obtained using Eq. (5) with  $\sigma = 0.065$  eV,  $N = 1 \text{ nm}^{-3}$ , and  $n/N = 1.6 \times 10^{-5}$ .  $\varepsilon_F$  is the Fermi level and  $\varepsilon_\infty$  is the thermal equilibrium energy, approaching  $-\sigma^2/k_B T$  at high temperatures. (b) Heat map of  $\varepsilon_{tr} - \varepsilon_\infty$  for a broad range of temperatures and exciton densities.

167  $n/N = 1.6 \times 10^{-5}$ , corresponding to one exciton in a lattice  
 168 of size  $(40 \text{ nm})^3$ , as implemented in our kMC simulations. The  
 169 same parameters were used in Fig. 2(a).

### 170 III. NONEQUILIBRIUM EXCITON DYNAMICS

#### 171 A. Demarcation energy level and energy relaxation

172 Having outlined the concept of the TE level and the gov-  
 173 erning equations for singlet exciton transport [50], let us now  
 174 turn our attention to the main problem, that is, the description  
 175 of the relaxation dynamics. Excitons, generated randomly  
 176 in the DOS, progressively thermalize into deeper energies.  
 177 Notwithstanding their way to the deep energy levels, excitons  
 178 need to be first activated to shallower energies, because the  
 179 density of such levels is high in the energy distribution. Using  
 180 the concept of the TE level we can say that these intermediate  
 181 activations, necessary to approach thermal equilibrium, are  
 182 most probable at the vicinity of the level  $\varepsilon_{tr}$ . As first introduced  
 183 by Tiedje and Rose [53], we can define a demarcation energy  
 184  $\varepsilon_m(t)$  in the system, such that during time  $t$  following the initial  
 185 excitation, only the levels with  $\varepsilon > \varepsilon_m(t)$  are likely to release

their excitons to the TE level. Mathematically, this means that  
 186  $t\nu(\varepsilon_m \rightarrow \varepsilon_{tr}) = \theta$ , with  $\theta$  being  $\mathcal{O}(1)$ . In a more explicit form,  
 187

$$t \frac{1}{\tau} \left( \frac{R_F}{R_{\varepsilon_{tr}}} \right)^6 \exp \left[ -\frac{\varepsilon_{tr} - \varepsilon_m(t)}{k_B T} \right] = \theta. \quad (6)$$

From the above equation we find

$$\varepsilon_m(t) = \varepsilon_{tr} - k_B T \ln \left[ \frac{t}{\theta \tau} \left( \frac{R_F}{R_{\varepsilon_{tr}}} \right)^6 \right]. \quad (7)$$

On the other hand, if we consider the low density condition, we  
 189 can obtain the following equation for the mean jump distance  
 190 from Eqs. (4) and (5):  
 191

$$\frac{1}{R_{\varepsilon_{tr}}^3} = \frac{8\pi}{3} g(\varepsilon_{tr}) k_B T. \quad (8)$$

Inserting Eq. (8) in Eq. (7), and using  $g(\varepsilon) = N/\sqrt{2\pi\sigma^2} \exp(-\varepsilon^2/2\sigma^2)$ , we get the following expression for  
 192 the demarcation level:  
 193  
 194

$$\varepsilon_m(t) = \varepsilon_{tr} \left( 1 + \frac{\varepsilon_{tr}}{\sigma^2/k_B T} \right) - k_B T \ln \left[ \left( N_F \frac{k_B T}{\sigma} \right)^2 \frac{2}{\theta \pi} \frac{t}{\tau} \right], \quad (9)$$

where  $N_F = (4\pi/3)R_F^3 N$ .

195 According to Eq. (9), in the course of time, the demarcation  
 196 level sinks to deeper energies. However, we note that this can  
 197 continue only until time  $t = \tau$ , which is the intrinsic lifetime  
 198 of the exciton. If we interpret the demarcation energy as a  
 199 quasi-Fermi level [54], at time  $\tau$  most excitons are accumulated  
 200 around an energy level at which the product  $g(\varepsilon)f[\varepsilon, \varepsilon_m(\tau)]$   
 201 maximizes. This energy is in fact the same energy  $\varepsilon_\tau$  shown  
 202 in Fig. 1.  $\varepsilon_\tau$  is in general different from  $\varepsilon_\infty$ , but if the  
 203 thermalization is completed during the exciton lifetime, we  
 204 obtain  $\varepsilon_\tau = \varepsilon_\infty$ . The energy,  $\varepsilon_\tau$  is experimentally available  
 205 through fluorescence spectroscopy. We stress that our model  
 206 can also be applied for exciton transport in the presence of  
 207 quenching centers [21,55]. In such a situation, one has to  
 208 consider the demarcation energy at time  $t < \tau$ .  
 209

The five energy levels discussed here,  $\varepsilon_{tr}$  (TE level),  $\varepsilon_\tau$  (en-  
 210 ergy relaxation during exciton lifetime),  $\varepsilon_m(\tau)$  (demarcation  
 211 or quasi-Fermi level at time  $t = \tau$ ),  $\varepsilon_\infty$  (thermal equilibrium  
 212 energy), and  $\varepsilon_F$  (equilibrium Fermi level), are plotted in Fig. 3  
 213 for  $R_F = 5 \text{ nm}$ . We have used  $\theta \approx 0.2$  since it gives excellent  
 214 agreement with kinetic Monte Carlo (kMC) simulations, see  
 215 below. As expected, at high disorder normalized temperatures  
 216 the thermalization is nearly complete, and therefore  $\varepsilon_\tau$  coin-  
 217 cides with  $\varepsilon_\infty$ . However, by decreasing  $k_B T/\sigma$ ,  $\varepsilon_\tau$  deviates  
 218 from  $\varepsilon_\infty$ , owing to the incomplete thermalization during the  
 219 exciton lifetime.  
 220

Two temperature regions in Fig. 3 need to be discussed in  
 221 detail. (i) Region with  $\varepsilon_m(\tau) > \varepsilon_\infty$ . The relaxation energy  $\varepsilon_\tau$  in  
 222 this region reaches a minimum at a critical temperature where  
 223  $\varepsilon_m(\tau) \approx \varepsilon_\infty$ , and then *increases* by decreasing the temperature,  
 224 see inset of Fig. 3. This behavior, usually assigned to frustrated  
 225 relaxation, has been observed experimentally [30,31], and has  
 226 been predicted through kMC simulations to occur also for  
 227 Förster energy transfer [38]. Here, we see that our model  
 228 can naturally produce the frustrated relaxation feature, see  
 229 Sec.III D for more details. (ii) Region with  $\varepsilon_m(\tau) > \varepsilon_{tr}$ . In the  
 230

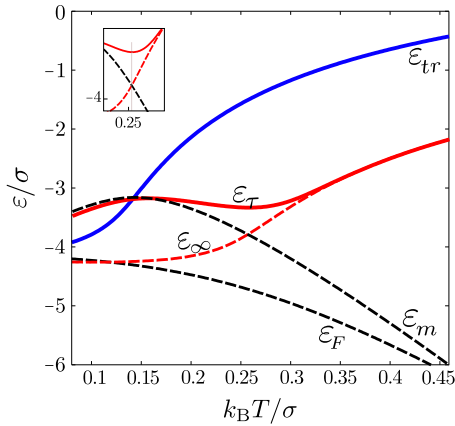


FIG. 3.  $\varepsilon_{tr}$  (TE level),  $\varepsilon_{\tau}$  (energy relaxation during the exciton lifetime),  $\varepsilon_m(\tau)$  (quasi-Fermi level),  $\varepsilon_{\infty}$  (thermal equilibrium energy), and  $\varepsilon_F$  (equilibrium Fermi level), as a function of disorder normalized temperature. Data are calculated using Eqs. (5) and (9) for  $R_F = 5$  nm.

temperature region given by the above condition, the multiple-trapping model is not applicable at all and introducing  $\varepsilon_m(\tau)$  is physically meaningless. In this region, excitons created in the system move, on average, downward toward the TE energy level, and therefore the picture of activation to a TE level is not correct. As we discuss below in the kMC section, an agreement between theory and simulation is not expected in this temperature region.

An important feature of the Förster-type transport mechanism is that the exciton transfer rate is coupled to the spontaneous decay rate,  $1/\tau$ ; see Eq. (1). Therefore, a longer exciton lifetime does not result in a higher degree of the thermalization, because the transfer rate, that determines the degree of thermalization, is also reduced. As a consequence, as predicted by Eq. (9), the demarcation energy at time  $t = \tau$ , and hence  $\varepsilon_{\tau}$ , are independent of the exciton lifetime. On the other hand,  $\varepsilon_{\tau}$  is a strong function of the Förster radius. We discuss this dependency below, when presenting the kMC simulation results.

### B. Exciton diffusion length

An important physical quantity related to exciton transport is the diffusion length. In what follows, we derive an expression for the exciton diffusion length using the TE level concept. Since the diffusion length is given by [56]

$$L_D = \sqrt{D\tau}, \quad (10)$$

we must first find the diffusion coefficient  $D$ . To obtain this, one can use [57]

$$D \approx R_{\varepsilon_{tr}}^2 / \langle t \rangle, \quad (11)$$

where  $\langle t \rangle$  is the mean time that excitons spend in an energy state before activation to the TE level.  $\langle t \rangle$  can be obtained by averaging the quantity  $1/\nu(\varepsilon \rightarrow \varepsilon_{tr})$  for energies smaller than

$\varepsilon_{tr}$  [57,58]:

$$\langle t \rangle = \tau \left( \frac{R_{\varepsilon_{tr}}}{R_F} \right)^6 \frac{\int_{-\infty}^{\varepsilon_{tr}} \exp\left(\frac{\varepsilon_{tr} - \varepsilon}{k_B T}\right) g(\varepsilon) f'[\varepsilon, \varepsilon_m(\tau)] d\varepsilon}{\int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) f'[\varepsilon, \varepsilon_m(\tau)] d\varepsilon}. \quad (12)$$

Combining Eqs. (10)–(12), as shown in Appendix B, we get the following expression for the diffusion length:

$$L_D \approx \left( \frac{9\theta^3}{16\pi^2} \frac{N' - n'}{n'^3} \right)^{1/6}, \quad (13)$$

where  $n' = \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) f[\varepsilon, \varepsilon_m(\tau)] d\varepsilon$  and  $N' = \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) d\varepsilon$ . Note that, since according to Eq. (9)  $\varepsilon_m(\tau)$  is a function of the Förster radius  $R_F$ , the diffusion length is also  $R_F$  dependent. However, it is clear from Eq. (13) that the dependency of  $L_D$  on  $R_F$  is more complex than that traditionally expected, that is,  $L_D \propto \sqrt{D} \propto \sqrt{\nu} \sim R_F^3$  (which is deduced from a simple nearest neighbor random walk picture). This is because, for the problem of exciton transport in energetically disordered systems,  $R_F$  is not merely a multiplicative factor, but according to Eq. (9), it also controls the thermalization process, which, in turn, affects the dispersivity of the diffusion process. Another important result of our theory, as discussed in Appendix C, is that both the quantity  $\varepsilon_{\tau}/\sigma$  and the diffusion length  $L_D$  in Eq. (13) scale with the dimensionless disorder strength  $\sigma/k_B T$ . Indeed, the scaling of both the exciton diffusion length and spectral relaxation has been predicted in the past by one of the authors using Monte Carlo simulations [19,39,59]. In the following section, we test the validity of our approach to the problem of nonequilibrium exciton transport against Monte Carlo simulations.

### C. Kinetic Monte Carlo simulations

Monte Carlo simulations provide an insightful and predictive computational method for studying incoherent hopping transport phenomena in disordered semiconductors. In this paper, we use a kMC method [19] to simulate the time evolution of singlet exciton transport, confirm the validity of the developed theoretical model and test its applicability range. The computational protocol is as follows.

We consider a regular cubic cell of  $40 \text{ nm} \times 40 \text{ nm} \times 40 \text{ nm}$  with a lattice constant  $a = 1$  nm. Each lattice point corresponds to an exciton transport site, while periodic boundary conditions are implemented along all directions of the cell using the minimum image criterion. Individual Monte Carlo runs start by placing one exciton at a random site in the cell with each site having an energy drawn from a Gaussian distribution with a zero mean and variance  $\sigma^2$ . Förster transfer rates  $\nu_{ij}$  from the exciton occupied site  $i$  to each neighboring hopping site  $j$ , within a cutoff radius of  $r_{\text{cut}} = 5$  nm, are calculated using Eq. (1). At each Monte Carlo step, waiting times for each hopping event are calculated according to  $\tau_{ij} = -\frac{1}{\nu_{ij}} \ln X$ , with  $X$  a random number from a box distribution from zero to unity, resulting in 514 events for the chosen cutoff radius. An additional waiting time for exciton recombination is computed as  $\tau_{tr} = -\tau \ln X$ . If the event with the shorter waiting time is a hopping event, then exciton transfers to the new site and

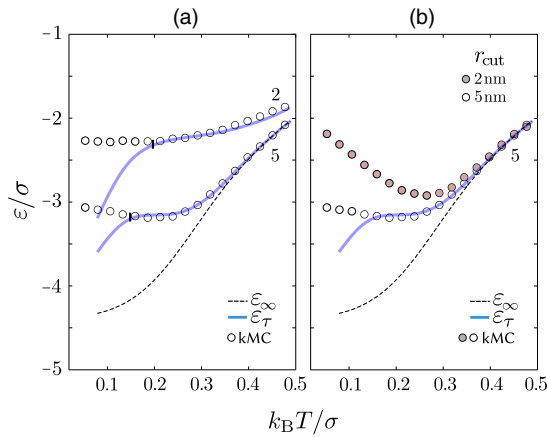


FIG. 4. (a) Energy relaxation during the exciton lifetime,  $\varepsilon_\tau$  as a function of disorder normalized temperature. kMC simulations (circles) and theory (solid lines), for two different Förster radii,  $R_F = 2$  and  $5$  nm. The critical points at which  $\varepsilon_m(\tau) = \varepsilon_{lr}$ , are indicated as segments. Dashed line indicates the thermal equilibrium energy  $\varepsilon_\infty$ . (b) Same as (a) with  $r_{\text{cut}} = 5$  nm (empty circles) and  $2$  nm (filled circles).

simulation advances whereas if it is recombination, the exciton is removed from the system and the run is terminated. By averaging over  $10^5$  individual exciton trajectories, we obtain the quantities of interest, i.e., the relaxation energy  $\varepsilon_\tau$  and the diffusion length  $L_D$ . The first is calculated from the final energy of each exciton before recombination, while the latter from the displacement between the initial, exciton generation, and the final, exciton recombination, position. We allow to vary independently the temperature  $T$  and Förster radius  $R_F$  parameters, while disorder  $\sigma$  and lifetime  $\tau$  remain constant. In fact, due to the Förster rate inverse dependence on  $\tau$ ,  $\tau$  does not impact neither the  $\varepsilon_\tau$  nor the  $L_D$  values, while a scaling law exists for both of them with respect to the dimensionless disorder parameter  $\sigma/k_B T$  [19,38].

The central results comparing theory with Monte Carlo simulations are presented in Fig. 4 for the spectral relaxation and Fig. 5 for the diffusion length. Figure 4(a) shows the Monte

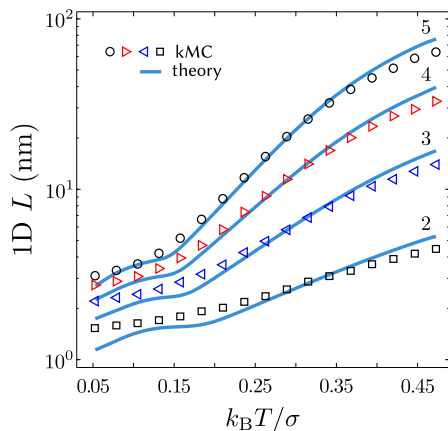


FIG. 5. Diffusion length  $L_D$  as a function of disorder normalized temperature. Data from kMC simulation (symbols) and theory (solid lines), for different Förster radii,  $R_F = 2, 3, 4,$  and  $5$  nm.

Carlo results for  $\varepsilon_\tau$ , for two Förster radii  $R_F = 2$  and  $5$  nm. The theoretical predictions, calculated based on the TE concept and using the averaging method (see Appendix D), are also shown in the figure. As pointed out above in Fig. 4(a), the multiple-trapping picture is not valid when  $\varepsilon_m(\tau) > \varepsilon_{lr}$ . The exact points at which  $\varepsilon_m(\tau) = \varepsilon_{lr}$  are calculated and marked in the figure. In the region where the TE concept is applicable, the theory is in very good agreement with the kMC results. Since the density of the energy levels is higher near the center of the Gaussian distribution, most excitons generated in the system will have energies  $\varepsilon \approx 0$  and according to the TE concept, those excitons initially move, *on average*, downward to the TE level  $\varepsilon_{lr}$ . However, en route to the TE level, some upward in energy jumps are also necessary to avoid the blockade of excitons due to disorder. Therefore, for larger Förster radii, the TE concept is valid over a broader range of temperatures, because a larger  $R_F$  results to a higher probability to overcome local energy barriers.

A recent combined experimental and computational study highlighted the dominant contribution of long-distance jumps to singlet exciton migration in metal-organic frameworks [60]. To illustrate the importance of long-distance hopping, we have also performed simulations with  $r_{\text{cut}} = 2$  nm (i.e., restricting exciton hopping only to the first 32 nearest neighbors). Figure 4(b) shows that in comparison to  $r_{\text{cut}} = 5$  nm (514 nearest neighbors), the energy relaxation shows a pronounced frustrated dynamics, inconsistent with the theory prediction. This clearly demonstrates that especially at low temperatures, long-range jumps contribute significantly to the relaxation process. In other words, due to the long-range nature of the Förster mechanism, modeling the singlet exciton transport as a simple nearest-neighbor random walk process may result in an incorrect description of the energy transfer dynamics. We can also conclude that for inherently short-range transport mechanism, like charge or triplet exciton transport problem, a strong frustration is expected, as indeed reported in earlier simulations [38,39]. We revisit this issue in more detail in Sec. III D, below.

Figure 5 compares  $L_D$  obtained from the kMC simulations with those calculated using Eq. (13). Apart from an additional constant factor ( $\approx 1.5$ ) needed to fit the theory to the simulation (see Sec. III E), the theoretical results are in good agreement with the kMC simulations showing a steep increase of the diffusion length with disorder normalized thermal energy. We point out that in contrast to spectral relaxation, reliable estimates for  $L_D$  from the theoretical model can be obtained even in the regime where  $\varepsilon_m(\tau) > \varepsilon_{lr}$  as  $L_D$  is less sensitive to  $\varepsilon_m(\tau)$  in that region. It must be noted that our results are in agreement with experimental reports on the temperature dependence of the exciton diffusion length [29,32]. Finally, Fig. 6 shows that the traditional picture of  $L_D \propto R_F^3$  does not hold true at the intermediate and low temperature region, as predicted and discussed in the theory section above.

#### D. TE level for short vs long-range transfer and comparison with experiment

Herein, we discuss the main differences on the TE level for short vs long-range excitation transfer and the resulting influence on energy relaxation. We also include a comparison

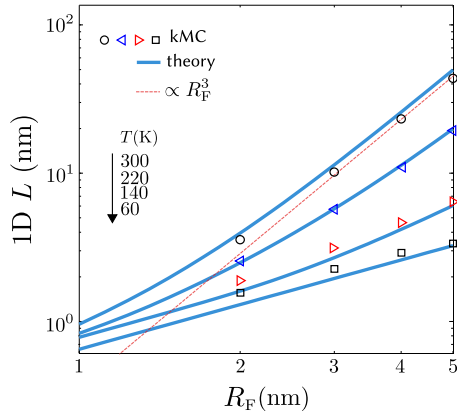


FIG. 6. Diffusion length  $L_D$  as a function of the Förster radius for different temperatures on a log-log scale. Data from kMC simulations (symbols) and theory (solid lines). Dashed line indicates the slope expected from  $L_D \propto R_F^3$ .

with published experimental data of temperature dependent fluorescence relaxation in organic semiconductors. Although in this paper we have focused on the hopping dynamics of singlet excitons that transfer by a Förster process, i.e., with a long-range transfer rate that is  $\propto \tau^{-1}(R_F/R)^6$ , within a Gaussian DOS, of particular interest is also the relaxation process of charge carriers and triplet excitons that follow a Dexter type of transfer mechanism. This short-range transfer process requires wave-function overlap and can be described by a Miller-Abrahams (MA) type of rate  $\propto \nu_0 \exp(-2R/\alpha)$ . An important difference between those two transfer mechanisms is that whilst for Förster transfer, exciton transport and decay are coupled to each other, due to the inverse dependence of the rate on the exciton lifetime  $\tau$ , for MA transfer the attempt to hop frequency prefactor  $\nu_0$  is independent of the lifetime, with typically  $\tau \gg \nu_0^{-1}$ .

The TE level has been used before to study energy relaxation of charges and triplet excitons that transfer by short-range hopping rate transfer [34,53,61]. Motivated by experimental observations of photoluminescence spectra [30,31] that show a nonmonotonic dependence of the relaxation energy upon cooling, those studies along with kMC simulations [34,38,39] have revealed that charges and triplet excitons show a strong frustrated relaxation, of the order of a few  $\sigma$ , as depicted schematically in Fig. 7(a). To describe this behavior, we first note that the TE level for short-range transfer (MA rate) [47,62] lies above the TE level for Förster transfer across the intermediate and low temperature range, as shown in Fig. 7(b). We highlight that for MA transfer,  $\varepsilon_{tr}$  is a function of disorder normalized thermal energy  $k_B T/\sigma$ , exciton density  $N$ , and localization length  $\alpha$  and is independent of  $\nu_0$ . For Förster transfer, however,  $\varepsilon_{tr}$  is only a function of  $k_B T/\sigma$  and is independent of  $N$ ,  $R_F$ , and  $\tau$ . The relative position of the pertinent TE levels is therefore valid for any combination of transport parameters, unless for very large, unrealistic values of  $\alpha$ . According to the multiple-trapping picture, upward excitation hops are mainly at the vicinity of the TE level. Henceforth, for short-range MA transfer, with decreasing thermal energy such

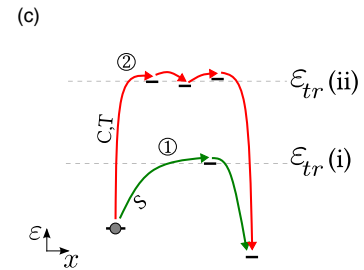
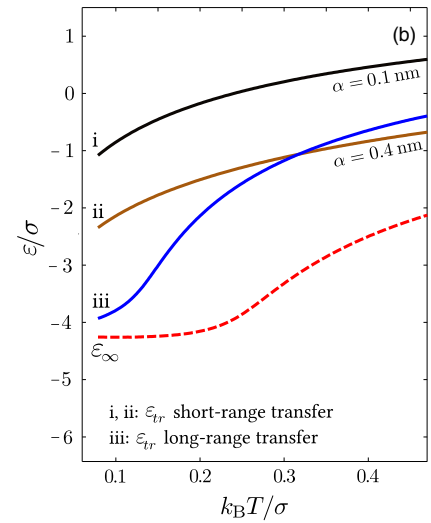
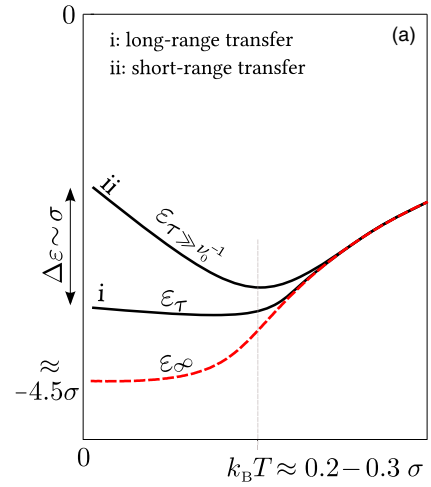


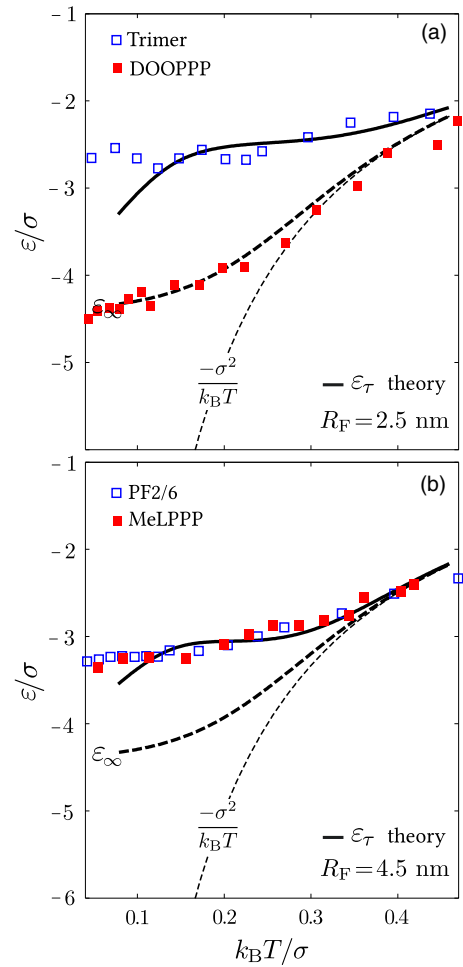
FIG. 7. (a) Illustration of temperature-dependent energy relaxation for long- vs short-range transfer processes. Short-range transfer (relevant for charges and triplet excitons) results in a strong frustration, of the order of  $\sigma$  at low temperatures. (b) Relevant ordering of temperature-dependent TE levels for long-range (Förster rate) and short-range (MA rate) transfer for typical transport parameters. (c) Schematic illustration showing the different relaxation pathways for charges and triplet excitons (C,T) and singlet excitons (S). The TE level for long-range transfer, i, lies below the TE level for short-range transfer, ii. Paths ① and ② result to relaxation toward deep energy levels. At intermediate and low temperatures, however, thermal activation via path ② is forbidden, leading to frustrated relaxation.

421 hops are less probable and the relaxation process terminates at  
 422 higher energies, because intermediate activations to the TE  
 423 level are necessary to reach the equilibrium level. This is  
 424 schematically shown in Fig. 7(c). On the other hand, since the  
 425 TE level for long-range Förster transfer is at lower energies,  
 426 thermal activations to this level are more likely and therefore  
 427 subsequent relaxation to deep energy levels is an allowed  
 428 process. Note that although for a Gaussian DOS, sites with  
 429 low energy levels are limited, the long-range nature of the  
 430 Förster rate makes upward energy jumps more probable for  
 431 singlet excitons [Path ① in Fig. 7(c)]. It is well established that  
 432 for disordered organic semiconductors and colloidal quantum  
 433 dots, a Gaussian DOS describes the distribution of localized  
 434 energy states [18], whereas for inorganic semiconductors an  
 435 exponential DOS is a more appropriate choice [34,61,63,64].  
 436 An important feature of the Gaussian DOS, in contrast to the  
 437 exponential one, is that for a broad temperature range the most  
 438 populated energy level ( $\varepsilon_\infty$  or  $\varepsilon_\tau$ ) does not lie near the Fermi  
 439 level ( $\varepsilon_F$  or  $\varepsilon_m$ ); see Fig. 3. Therefore, for calculating the  
 440 amount of the energy relaxation, we have used the energy  
 441  $\varepsilon_\tau$  and not the demarcation energy  $\varepsilon_m$ . For an exponential  
 442 DOS however, since  $\varepsilon_{\infty(\tau)} \simeq \varepsilon_{F(m)}$ , one can use the position  
 443 of the demarcation energy as the energy relaxation, as done in  
 444 Refs. [34,61] for short-range type of transfer in an exponential  
 445 DOS.

446 Finally, we compare our theoretical results for the energy  
 447 relaxation ( $\varepsilon_\tau$ ) based on the TE level formulation with previ-  
 448 ously published experimental data in conjugated polymers and  
 449 oligomers. Figure 8 shows experimental data obtained from  
 450 the fluorescence spectra of four different films: dioctyloxy-  
 451 poly(*p*-phenylene) (DOOPPP), polyfluorene (PF2/6), ladder-  
 452 type poly(*p*-phenylene) (MeLPPP), and PF2/6 trimer (Trimer)  
 453 as reported in Refs. [30,38]. It is evident that the theory  
 454 reproduces the experimental data for reasonable Förster radii  
 455 (best fits are obtained with  $R_F = 2.5$  and 4.5 nm, as indicated  
 456 in the figure). Note that according to Eq. (9), the quantity  $N R_F^3$   
 457 is the fit parameter. Here, however, we have decided to fix the  
 458 total density of states ( $N = 1 \text{ nm}^{-3}$ ) and only vary the Förster  
 459 radius to obtain the above data. In Fig. 8, in addition to  $\varepsilon_\tau$ ,  
 460 we also display  $\varepsilon_\infty$  (energy relaxation at equilibrium) and the  
 461 quantity  $-\sigma^2/k_B T$ . Interestingly, the equilibrium quantity  $\varepsilon_\infty$   
 462 fits the experimental data for the DOOPPP polymer over the  
 463 whole temperature range, showing that singlet excitons reach  
 464 equilibrium conditions during their lifetime. This, in turn, is  
 465 a result of the high density of localized states, a large Förster  
 466 radius, or a combination of these two factors.

### 467 E. Subdiffusive transport

468 Having established the effectiveness of the analytical model  
 469 to describe spectral relaxation, we now turn our attention  
 470 to obtaining the time dynamics of exciton diffusion. Very  
 471 recently, it has been reported experimentally that exciton  
 472 diffusion in a system of disordered colloidal quantum dots is  
 473 dispersive and can be described as a subdiffusive transport  
 474 [3], in which  $D(t) \propto t^\beta$  with  $\beta < 0$ . Similar results have been  
 475 obtained from Monte Carlo simulations for triplet exciton and  
 476 charge transport in a Gaussian DOS [39,65]. To investigate  
 477 whether our model can explain these observations, we expand  
 478 the TE concept to take into account the time dependence of the



479 FIG. 8. Energy relaxation during the exciton lifetime,  $\varepsilon_\tau$  as a  
 480 function of disorder normalized temperature. Theoretical data based  
 481 on the TE level (solid line) and experimental data obtained from the  
 482 fluorescence spectra of (a) PF2/6 trimer (empty squares) and DOOPPP  
 483 polymer (filled squares) films (from Ref. [30]) and (b) PF2/6 (empty  
 484 squares) and MeLPPP (filled squares) polymer films (from Ref. [38]).  
 485 The Förster radii  $R_F$  used in the calculations are indicated in the plots.  
 486 The levels  $\varepsilon_\infty$  (thick dashed line) and  $-\sigma^2/k_B T$  (thin dashed line) are  
 487 also plotted.

479 dynamics for  $t < \tau$ . This can be achieved by considering  
 480 the demarcation energy  $\varepsilon_m(t)$ , instead of  $\varepsilon_m(\tau)$  used in the  
 481 previous calculations. Below, we present results for the energy  
 482 relaxation shift  $\varepsilon_{t \leq \tau}$  and the diffusion coefficient  $D(t)$ , while  
 483 we derive the time-dependent expressions in Appendix B.

484 Figure 9 shows the temporal evolution of  $\varepsilon_{t \leq \tau}$  and  $D(t)$  for  
 485 two different temperatures and two Förster radii,  $R_F = 2$  and  
 486 5 nm. As seen in Fig. 9(a), in the course of time, excitons relax  
 487 to lower energy levels. For a Förster radius of  $R_F = 5$  nm and  
 488 at high temperatures, excitons reach the equilibrium energy  
 489 during their lifetime [this is also apparent in Fig. 4(a)] and  
 490 a stationary state is indeed established at  $t < \tau$ . In contrast,  
 491 at low temperatures and/or small Förster radius, the relaxation  
 492 process is incomplete and the stationary state can not be obtained.  
 493 Interestingly, our theoretical results for low temperatures  
 494 show a linear dependence with time in the logarithmic scale  
 495  $\varepsilon_{t \leq \tau} \sim -\ln(t/\tau)$ , with the same slope for both  $R_F = 2$  and



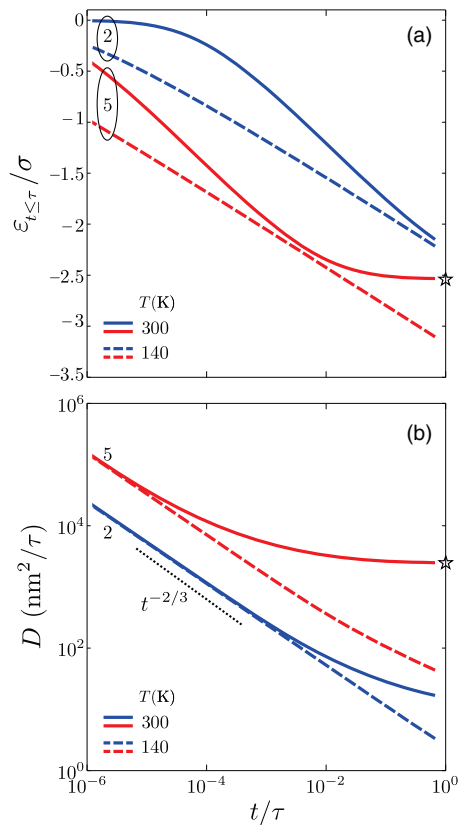


FIG. 9. (a) Energy relaxation (shift) as a function of time. Data for  $T = 140$ , and  $300$  K, and  $R_F = 2$  and  $5$  nm. (b) Diffusion coefficient  $D(t)$  as a function of time calculated using Eq. (B5). Data for  $T = 140$  and  $300$  K and  $R_F = 2$  and  $5$  nm. The dotted line shows the scaling of the diffusion coefficient with time in the nonequilibrium regime. Stars indicate the equilibrium values.

5 nm, and are in agreement with results from Movaghar *et al.* [51]. The time evolution of the diffusivity is shown in Fig. 9(b). As a result of exciton relaxation to lower energy levels with time, based on the multiple-trapping picture, the waiting time needed to jump to the TE level increases with time. Therefore, the diffusion coefficient becomes time-dependent, i.e., dispersive transport, and decreases with time. As derived in Appendix B, in this nonequilibrium regime we obtain

$$D(t) \propto \left(\frac{t}{\tau}\right)^{-2/3}, \quad (14)$$

which clearly demonstrates the dispersive nature of singlet exciton diffusion. Nevertheless, at high temperatures and large Förster radius, since equilibrium can be established during the exciton lifetime, the diffusion coefficient approaches its equilibrium, time-independent, value.

In obtaining Eq. (13) for the diffusion length, the diffusion coefficient at time  $t = \tau$  has been used in the calculations. However, since the exciton transport occurs almost entirely in the nonequilibrium regime and the diffusion coefficient is time-dependent, using  $D(t = \tau)$  may result in an underestimation of the diffusion length. This argument shows why an additional factor was required to fit the theory with the kMC results in Fig. 5. One can estimate this factor by using the following

relation for the diffusion length of excitons :

$$L_D = \sqrt{\int_0^\tau D(t) dt}. \quad (15)$$

Using Eq. (14) we have

$$L_D \approx \sqrt{D(\tau)\tau \int_0^\tau (t/\tau)^{-2/3} d(t/\tau)} = \sqrt{3} \times \sqrt{D(\tau)\tau}. \quad (16)$$

The factor  $\sqrt{3}$  justifies the additional factor used in Fig. 5 to match the theory with the kMC results.

#### IV. CONCLUSION

A theory for singlet exciton hopping transport has been developed and tested. It describes diffusive transport via long-range Förster transfer in a Gaussian distribution of localized states through a multiple-trapping mechanism, with the TE playing the role of the mobility edge. The theory provided in this paper fully describes the transition from equilibrium to nonequilibrium transport. The global validity range of the theory is illustrated by comparison to Monte Carlo simulations. We find that for Förster radius values smaller than 5 nm, typical in organic semiconductors, exciton transport occurs mainly in the nonequilibrium regime and the diffusion length deviates from the cubic dependence upon the Förster radius. An important feature of the theory is that it takes into account explicitly the temporal evolution of the spectral relaxation energy and diffusivity and can be used to understand time-gated spectroscopic experiments in a wide range of disordered semiconducting materials. Understanding the exciton dynamics is also important for exploiting novel device applications. In the current paper, we take a step toward this goal and anticipate that it will motivate further studies. In future work, we hope to tackle the excitation density dependence of the relaxation dynamics and transport in spatially correlated disordered systems.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: POSITION OF THE TRANSPORT ENERGY

According to Eq. (1), the upward exciton jump rate is given by

$$v(\varepsilon_d \rightarrow \varepsilon_a) = \frac{1}{\tau} \left(\frac{R_F}{R}\right)^6 \exp\left(-\frac{\varepsilon_a - \varepsilon_d}{k_B T}\right), \quad (A1)$$

where  $\varepsilon_a - \varepsilon_d > 0$  is the difference between the acceptor and donor energy. Let us denote this rate by  $\nu_\uparrow(\varepsilon_d, \varepsilon_a, R)$ . For steep energy distributions, the typical upward jump distance is given

559 by [Eq. (4) in the main text]

$$R_{\varepsilon_a} = \left[ \frac{4\pi}{3} \int_{-\infty}^{\varepsilon_a} g(\varepsilon) f'(\varepsilon, \varepsilon_F) d\varepsilon \right]^{-1/3}. \quad (\text{A2})$$

560 Now, according to the standard approach of calculating the TE  
561 level, we seek to find if such an acceptor energy level exists  
562 that it maximizes all typical upward jumps, independent of the  
563 donor energy. In other words, we look for a unique acceptor  
564 energy,  $\varepsilon_{tr}$ , that meets the condition

$$\left. \frac{\partial v_{\uparrow}(\varepsilon_d, \varepsilon_a, R_{\varepsilon_a})}{\partial \varepsilon_a} \right|_{\varepsilon_a = \varepsilon_{tr}} = 0. \quad (\text{A3})$$

565 By algebraic manipulation of the above equation, we obtain  
566 Eq. (5).

### 567 APPENDIX B: DIFFUSION COEFFICIENT

568 In this appendix, a general expression for the diffusion  
569 coefficient is obtained, from which the time-dependency of  
570 the diffusion coefficient and the singlet diffusion length can be  
571 extracted. First, we note that the integral in the numerator of  
572 Eq. (12) can be rewritten as

$$\exp\left(\frac{\varepsilon_{tr} - \varepsilon_m}{k_B T}\right) \int_{-\infty}^{\varepsilon_{tr}} \exp\left(\frac{\varepsilon_m - \varepsilon}{k_B T}\right) g(\varepsilon) f'(\varepsilon, \varepsilon_m) d\varepsilon, \quad (\text{B1})$$

573 where, for brevity, we have used  $\varepsilon_m$  for  $\varepsilon_m(t)$ . This, bearing in  
574 mind that  $f' = 1 - f$ , can be simplified as

$$\exp\left(\frac{\varepsilon_{tr} - \varepsilon_m}{k_B T}\right) \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) f(\varepsilon, \varepsilon_m) d\varepsilon. \quad (\text{B2})$$

575 On the other hand, using Eq. (6), for the exponential term in  
576 the above equation we have

$$\exp\left(\frac{\varepsilon_{tr} - \varepsilon_m}{k_B T}\right) = \frac{t}{\tau \theta} \left( \frac{R_F}{R_{\varepsilon_{tr}}} \right)^6. \quad (\text{B3})$$

577 Using these simplifications, and if we define  
578  $n' = \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) f(\varepsilon, \varepsilon_m) d\varepsilon$  and  $N' = \int_{-\infty}^{\varepsilon_{tr}} g(\varepsilon) d\varepsilon$ , we obtain

$$D(t) = \frac{\theta}{t} R_{\varepsilon_{tr}}^2 \frac{N' - n'}{n'}, \quad (\text{B4})$$

579 that, using Eq. (4), can be rewritten as

$$D(t) = \frac{\theta}{t} \left( \frac{4\pi}{3} \right)^{-2/3} \frac{(N' - n')^{1/3}}{n'}. \quad (\text{B5})$$

580 From this general result, one can obtain Eq. (13) for the  
581 diffusion length  $L_D = \sqrt{D(\tau)\tau}$ .

582 To obtain the time-evolution of the diffusion coefficient in  
583 nonequilibrium regime, we use the fact that the demarcation  
584 energy is high at short and intermediate times such that we can  
585 write  $f \approx 1$  and  $1 - f \approx \exp\{[\varepsilon - \varepsilon_m(t)]/k_B T\}$ . Therefore,  
586 since  $\varepsilon_m(t) = \varepsilon_m(\tau) - k_B T \ln(t/\tau)$ , we can obtain the follow-  
587 ing time-dependent behavior for the diffusion coefficient (valid  
588 only for the nonequilibrium regime):

$$D(t) \propto (t/\tau)^{-2/3}. \quad (\text{B6})$$

589 On the other hand, at the equilibrium regime where the  
590 demarcation energy lies deep in the energy distribution, we

can use the approximation  $f \approx \exp\{-[\varepsilon - \varepsilon_m(t)]/k_B T\}$  and  
 $N' - n' \approx N'$ . These approximations result in a stationary  
diffusion coefficient as

$$D_{st} \propto (t/\tau)^0. \quad (\text{B7})$$

### 594 APPENDIX C: SCALING BEHAVIOR OF THE 595 DIFFUSION LENGTH

Equation (3) shows that at a given density  $n$ , the Fermi level  
 $\varepsilon_F$  is determined by the temperature and the width of the energy  
distribution. By expressing this integral in terms of a new  
variable  $x = \varepsilon/\sigma$ , we find that the temperature-normalized  
Fermi level, that is,  $\varepsilon_F/k_B T$ , is a function of the dimensionless  
disorder parameter  $\sigma/k_B T$ . Using this result, and the same  
change-of-variable for the integral of Eq. (5), we find that  
 $\varepsilon_{tr}/\sigma$  is a function of  $\sigma/k_B T$ . Inspection of Eq. (9) for the  
demarcation level shows that the same scaling behavior holds  
for  $\varepsilon_m(\tau)/\sigma$ , and since  $\varepsilon_{\tau}$  is the energy at which the product  
 $g(\varepsilon)f[\varepsilon, \varepsilon_m(\tau)]$  maximizes, we find that  $\varepsilon_{\tau}/\sigma$  also scales with  
 $\sigma/k_B T$ . Using the above scaling features and Eq. (13), we  
obtain that  $L_D = L_D(\sigma/k_B T)$ .

### 609 APPENDIX D: AVERAGING METHOD FOR THE 610 CALCULATION OF THE RELAXATION ENERGY

The equilibrium energy  $\varepsilon_{\infty}$  can be calculated in two  
different ways. As pointed out in the main text, we have  
introduced  $\varepsilon_{\infty}$  as the energy that maximizes the product  
 $g(\varepsilon)f(\varepsilon, \varepsilon_F)$ . Accordingly, the relaxation energy  $\varepsilon_{\tau}$  can be  
found by maximizing the product  $g(\varepsilon)f[\varepsilon, \varepsilon_m(\tau)]$ . On the  
other hand, one can define the equilibrium or relaxation energy  
as the average energy of the carriers. In this definition, the  
equilibrium energy is calculated as

$$\langle \varepsilon \rangle = \frac{\int \varepsilon g(\varepsilon) f(\varepsilon, \varepsilon_F) d\varepsilon}{\int g(\varepsilon) f(\varepsilon, \varepsilon_F) d\varepsilon}. \quad (\text{D1})$$

To obtain  $\varepsilon_{\tau}$ , one needs to replace  $\varepsilon_F$  with  $\varepsilon_m(\tau)$  in the  
above equation. We find that the averaging method gives  
excellent agreement with Monte Carlo simulations. In compar-  
ison, the method of maximizing the product  $f \times g$  results in  
slightly lower values for the equilibrium energy at intermediate  
and higher temperatures and a more pronounced minimum  
(Fig. 3). However, since the product  $f \times g$  is approximately  
a symmetric function of energy, the two definitions result in  
the same overall trend and similar values for the relaxation  
energy. From a practical point of view, while the first method  
is numerically more tractable, the second definition is most  
suitable for comparing with kMC simulation results, where  
the relaxation energy is obtained by averaging over different  
exciton trajectories. Throughout this paper, we adopted the  
first method, except in Figs. 4 and 8 where we compare  $\varepsilon_{\tau}$   
with kMC calculations and experimental results.

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